

THE IMPORTANCE OF BASICITY IN GLASS MELTS AND ATTEMPTS AT
ITS MEASUREMENT. PART I

W. Stegmaier and A. Dietzel

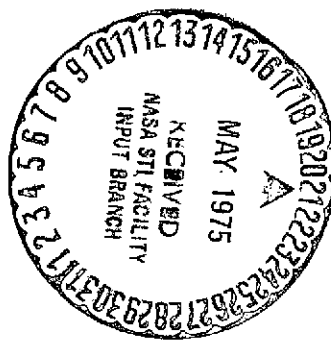
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THE IMPORTANCE OF BASICITY IN GLASS MELTS AND ATTEMPTS
AT ITS MEASUREMENT. PART I

W. Stegmaier* ** and A. Dietzel*

ABSTRACT. The concepts of "acid" and "base" have for a long time been in use for glass, ceramic materials, and the like, although there is no exact understanding of the meaning of basicity for glasses, let alone a possibility of comparing or quantitatively measuring basicity. The present investigation uses the concentration of oxygen ions as the scale to define the basicity of glass melts. Several examples (dyes, solubility, compound-forming or slag-forming capacity, gas absorption) show the influence of different basicities in glasses, or of the "strength" of the bases or acids. We compare the basicities in different materials with the aid of color indicators, and finally track them electrochemically through changes in the concentration of oxygen ions in the case of Li, Na, and K borate glasses. The results are of interest for an understanding of the constitution of these glasses.

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I. Introduction and Definition of Problem

The concepts of "acid" and "basic" for certain groups of combinations of materials as used in glass technology and ceramics are mostly based on phenomena one knows from hydrous solutions. For instance, in ceramics, a clay is called "acid" if it contains about 20 to 25% alumina or less and, correspondingly, at least 75% silicic acid, the latter either in bound form or in the form of free quartz. Clay is called "basic" if it contains at least 30 to 35% alumina, up to the maximum of 40% in the case of pure kaolinite. Other ceramic materials have been treated in the same fashion: silica stone, with its average of 95% SiO_2 , is called a "highly acid" stone; sillimanite or mullite stones, with their 60% or even more than 70% alumina, are "highly basic". Ordinary technical glasses are called "acid" if their percentage of silicic acid, boric acid, phosphoric acid (or even alumina) together amounts to 80% or more, whereas "basic" glass melts are those with less than about 75% acid oxides, or more than 18 to 20% alkali. Thus, as we can see from these examples, the concepts are applied to crystallized as well as to vitreous states, and so far have been based essentially on the gross chemical composition; differences in constitution are, in general, not taken into account. The basis for this type of definition is obviously the average range of technologically useful compositions, that is, in the case of glasses, the range of about 10 to 20% alkali, 0 - 10 or 15% $\text{RO} + \text{R}_2\text{O}_3$, with the remainder silicic acid, boric acid, etc.

Thus, silicon chemistry has taken over the concepts of "acid" and "basic" from the chemistry of hydrous solutions, and it is remarkable that it has not made use of the concept of a neutral point; nobody would understand without further explanation what is meant by a "neutral" clay, or a "neutral" glass. The older literature on glass technology refers to a "normal" glass, which in essence corresponds to such a hypothetical "neutral" glass.

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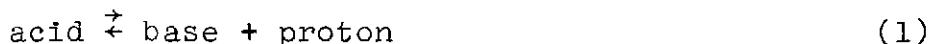
Our discussions and investigations intend to detail the concepts of "acid" and "basic" in the case of glass melts, to look for relations between basicity and some physicochemical properties of simple glass systems, to define a quantitative scale for basicity, and, finally, to compare the basicity of some of those simple glass systems.

II. Theoretical Part

A. Discussion of the concepts of "acid" and "base"

Originally, the concepts of "acid" and "base" were defined for hydrous solutions only, but recently, they were applied to some non-hydrous solvents, such as NH_3 ; SO_2 , and others. We shall discuss the solvents in this order, and then finally turn to the glass melts.

1. Water as solvent. Svante Arrhenius [1] arrived at the following definition in the framework of his classical theory of dissociation: An acid is a material which gives off hydrogen ions in hydrous solution, whereas a base is a material which gives off OH ions if it, too, is in hydrous solution. I. N. Brönsted [2] has extended this theory in 1923, and developed a more general definition of acids and bases which, presumably, is independent of the solvent. This scheme reads:

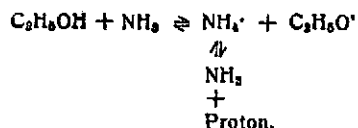


Here, the concepts of acid and base are defined simultaneously. To quote an example, NH_3 is a base, according to Brönsted, since from (1) we see that it is able to attach protons:



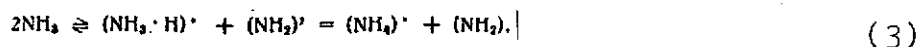
The protons to be attached are obtained by the ammonia from the solvent, such as water, alcohol, etc., that is, from any solvent that can give off protons. Thus, we understand that NH_3 is a base, even

with alcohol as solvent; however, only with Brönsted's, but not with Arrhenius', definition:

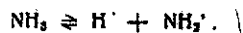


In this case, we see no OH ions which, in the classical theory, were characteristic for a base.

2. Non-hydrous solutions. Even a few non-hydrous liquids are known to be excellent solvents for anorganic dissociable compounds. For instance, liquid ammonia behaves in much the same fashion as water, as far as its dissolving capacity and the chemistry of such solutions are concerned. Similar behavior patterns are shown by hydrazine, liquid hydrogen sulfide, phosgene, anhydrous hydrofluoric acid, and, in particular, liquid sulfur dioxide. As is the case with water, ammonia is dissociated only to a small percentage. Here, the scheme reads:

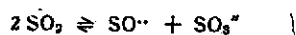


or:

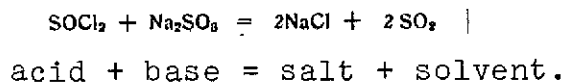


This means that if we have ammonia as solvent, materials that give off a proton in the solvent should be called acids, according to the definition by Brönsted.

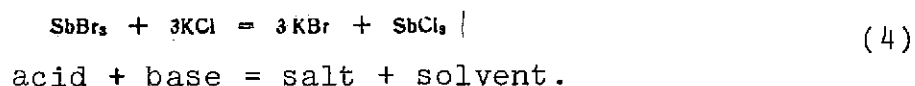
Brönsted's theory, however, fails in the case of those solvents that cannot give off any more H^+ ions. An important solvent of this type is SO_2 , which has been investigated in detail, for instance, by G. Jander and K. Wickert [3], and by K. Wickert and G. Jander [4]. To a small percentage, it is dissociated according to the relation:



K. Wickert [5] has investigated neutralization reactions in SO_2 as solvent; for instance, the reaction:



Here, SOCl_2 plays the part of the acid, Na_2SO_3 — the part of the base. K. Wickert [6] discusses yet another solvent, namely, SbCl_3 , and neutralization reactions of the type:



In both cases, no proton ever appears, and Brönsted's definition of acids and bases is not applicable. Thus, Wickert defined, for all the systems we discussed, new and more general relations for acids and bases that are independent of the type of solvent; he restricted his considerations in this endeavor to "water-like" solvents. He states that:

1. "An acid is a substance which, if dissolved in a water-like solvent, results in dissociation products consisting of a negative ion with closed electron configuration. The positive ion must be identical with the positive ion of the solvent.
2. "A base is a substance which dissociates in a water-like solvent, and whose dissociation products consist of a negative ion with closed electron configuration and a positive ion which also has a closed electron configuration." The negative ion must be identical with the negative ion of the solvent.
3. "A salt is a chemical compound in any solvent, if in solution it dissociates more or less into positive and negative ions, such that the ions have a closed electron configuration; no ion is identical with the electrolytic decomposition product of the solvent.

4. "A solvent is water-like, if it dissociated more or less into positive and negative ions, but only the negative ion has a closed electron configuration."

In the last example (4), SbBr_3 is the acid, since it dissociates into SB^{+++} (no closed outermost electron shell) and 3Br^- (outermost shell is closed). Moreover, the positive SB^{+++} ion is equal to the positive dissociation product of the solvent SbCl_3 . The other substances (bases, etc.) can be similarly classified.

However, one can also formally read Equation (4) in the opposite direction. Then, SbCl_3 is the acid, KBr — the base, KCl — the salt, and SbBr_3 — the solvent. All this is in complete agreement with Wickert's definitions. Hence, we see that the concepts cannot be separated completely, but that in most cases, the part of the acid and that of the solvent in a given system can be reversed, and that similarly, base and salt can exchange roles. In general, that substance (of the two possible candidates) is called the solvent which makes up most of the material.

It should be noted that Wickert puts a certain emphasis on the condition that his solvents are "water-like". The water-like solvents and other types of solvents that might be present then differ in that the water-like solvents have ions with open electron configurations among their dissociation products. This indeed is the case with the solvents we discussed, namely, the positive ions H^+ , NH_4^+ , SO^{++} , and Sb^{+++} . However, there are several substances that do not satisfy this condition, and still can take the part of the solvent. For example, liquid SO_3 , SnCl_4 , B_2O_3 , or borates, etc., are not water-like solvents, since they are unable to dissociate in such a fashion that a positive ion with a closed electron configuration appears. All these cases would have to be called "water-unlike solvents" according to Wickert. If one looks more closely at this problem, one concludes that the solvents Wickert calls "water-like"

consist of H^+ or of elements whose valence differs from the one, according to their position in the periodic system, e.g.:

sulfur, group 6, but tetravalent in SO_2 ;

nitrogen, group 5, but trivalent in NH_3 ;

antimony, group 5, but trivalent in $SbCl_3$.

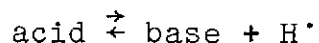
Wickert himself has not drawn these conclusions; however, they are interesting for further work in this area.

If one wants to summarize the facts known to date, one would conclude that neutralization reactions of the type acid + base = salt + solvent occur only in water-like solvents.

3. Molten salts and enamels. H. Lux [7] recently attempted to define the concepts of "acid" and "base" in melts of the oxide type by formulating the relation:



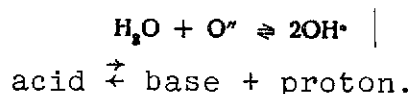
His starting point was the relations:



or

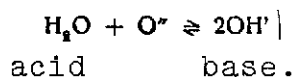


In melts of the oxide type, the O'' ion takes the part of the OH' ion in hydrous solutions. That this correspondence is correct is seen from the following consideration: According to Brönsted, water is a weak acid, since it dissociates in such a manner that, to a small degree, protons appear as dissociation products. The scheme reads:



According to Lux and Equation (5), one could write down the formally analogous scheme:

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According to Brönsted's definition, a NH_4^+ ion, for instance, must be considered an acid, since it gives off a proton by the formation of NH_3 (base); according to Lux, one would have to write:



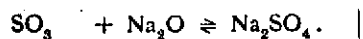
or



A salt, such as Na_2SO_4 , in a melt can be thought of as dissociated in either one of two ways: first, into ions, according to the relation:

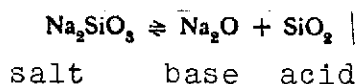


or else, thermally, according to the relation:

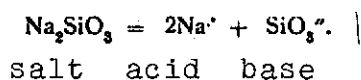


In both cases, the salt Na_2SO_4 is split into an acid and a base.

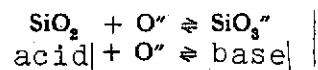
As with Na_2SO_4 , one can formulate a dissociation of silicates, borates, or glasses, according to the scheme:



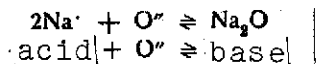
or, respectively,



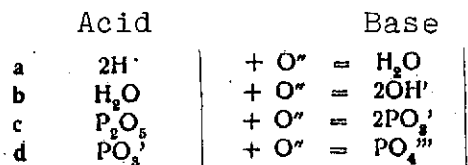
There is no doubt that in this case, SiO_2 is an acid, since we can write:



On the other hand, Na_2O would be a base, since:



To understand the importance of this terminology, we quote some examples. The following set of reactions occur:



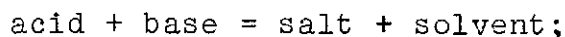
Thus, it follows that in case a), water is a base; in case b) — an acid.

The same is true for PO_3^+ in schemes c) and d). As a matter of fact, the concepts of "acid" or "base", using these considerations, are then uniquely applicable if one looks in each case only at the partial systems. That is, in the system $\text{P}_2\text{O}_5 - \text{NaPO}_3$, the former is, without doubt, the acid, the latter — the base; in the system $\text{NaPO}_3 - \text{Na}_2\text{PO}_4$, on the other hand, the metaphosphate plays the part of the acid, etc. It becomes obvious now that at least at first glance, the concepts of "acid" and "base" are completely relative. Thus, such definitions mean little for the actual chemical behavior of the so-defined "acids" or "bases". In fact, for example, it is not clear what type of substance is formed by combining the "acid" Na^+ with the "base" OH^+ ; would it be a salt?

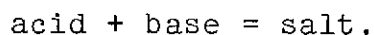
This large uncertainty exists because, as yet, it is impossible to attach to acids or bases "ordering numbers", or even numerical values for their "strengths". Now, if the concepts of "acid" or "base" are not clear, then a fortiori the definition of a neutral point is impossible.

As far as the glass melts are concerned, we must realize that SiO_2 , B_2O_3 , etc., are the acids, Na_2O , CaO , etc. — the bases. Somewhere in between, there is a neutral point. H. Salmang [8] has stated his opinions concerning such a neutral point on the basis of observations of slagging with fireproof building materials. He claims that the neutral point corresponds to the combination $\text{RO}:\text{SiO}_2 = 1 : 1$. If the content of bases is higher, the corrosion by the slags is much stronger than if the ratio is below unity; thus, at the equality ratio, a saturation of acids and bases is supposed to be reached. If we consider, for comparison, the corresponding situation in the case of hydrous solutions, we expect to find the following: Only by chance will the neutral point be at the position of a stoichiometric combination; in fact, at present we have no way of measuring its position with any accuracy, but rather profess a feeling for this position. In most cases, the neutral point will be found shifted toward the acid or the base, as compared with the case of the "neutral salt", depending on the "strengths" of the acid and the base that take part in the reaction. Thus, one could expect to find for glasses similar situations, as encountered — for instance, with phosphates — where one distinguishes an acid salt NaH_2PO_4 , a neutral Na_2HPO_4 , and a base Na_3PO_4 , with the stoichiometric neutral point placed at Na_3PO_4 .

To conclude these considerations, we want to emphasize a few more points. In water-like solvents of the type we discussed, the neutralization reactions go according to the scheme:



by contrast, the neutralization reactions in melts appear to be of the type:



There is no solvent; instead, the molten salt itself or a mixture of salt and excess acid or base, respectively, takes on the part of the solvent. We shall come back to this point later.

However, there is a completely different explanation of the basicity behavior in contrast to what we have developed so far: SiO_2 , B_2O_3 , etc., do not play the role of a true acid, but rather of a solvent, that is, they are comparable to water. Then, all known types of glass are in the alkaline range. In this case, even the neutral point, namely, pure SiO_2 , etc., is defined. However, the question arises as to the definition of an acid in such a system. We have addressed this question as well in the present investigation.

It has also been said that glass melts are really a special group among the molten salts, in the sense that they are dissolved into each other. Now, a discussion of glass basicity becomes meaningless.

B. Relations between basicity and the physicochemical properties of simple glass systems

Let us start with the question we just raised, namely, as to whether it is appropriate at all to speak of "acids" and "bases" or of melts of different basicity, in the case of glass melts; perhaps, /300 in reality, we simply deal with molten salts and their mutual solutions. Thus, in the following, we first discuss some relations and phenomena that can be most easily explained by assuming a different basicity of the melts.

1. Melting diagrams and basicity. If one adds to the melt of a substance, such as silicic acid, boric acid, and the like, increasing amounts of a basic oxide, then the melt reaches sooner or later a region where the first stable compound, such as a silicate or a borate, precipitates at lower temperatures in crystalline form. It is even possible to estimate from the behavior of the melting curve or from the type of melting process (whether it is congruent or incongruent), whether the compound can be assumed as present, at least to a certain degree, even in the melt. If one now varies the bases (Na_2O , K_2O , CaO , BaO , etc.), and if this stage of first compound formation which corresponds to the highest acidity occurs at a

different molar ratio of base to SiO_2 , P_2O_5 , then it can be concluded simply on the basis of chemistry that these bases are able to bind silicic acid, etc., to a varying degree. Thus, we would have a measure for their "strength".* The argument goes as follows: If, for instance, in the case of silicate systems**, the compounds with the highest molar ratio of silicic acid to basic oxide are selected, the following table is obtained:

System	Molar ratio SiO_2 /base for the highest degree of acidification
$\text{SiO}_2 - \text{ZnO}$	1 (incongruent melting)
$\text{SiO}_2 - \text{Al}_2\text{O}_3$	1 (incongruent melting)
$\text{SiO}_2 - \text{MgO}$	1 (congruent melting)
$\text{SiO}_2 - \text{CaO}$	1
$\text{SiO}_2 - \text{SrO}$	1

(Table continued on following page)

* This interpretation of the concept of the "strength" of a base is somewhat unusual, and does not immediately appear to agree with the understanding on the basis of the chemistry of hydrous solutions; see above. However, one can find examples even here: The ability of the alkali fluorides to attach HF increases markedly from Li to K. This is seen in the fact that the presently known highest "stages of acidity" are $\text{LiF} \cdot \text{HF}$ and $\text{NaF} \cdot \text{HF}$, while we have $\text{KF} \cdot 4\text{HF}$ and also $\text{RbF} \cdot 3\text{HF}$. In addition, the stability of the difluorides increases from Li to Na, K, and Rb. (The details are given in Gmelin's handbook, 8th edition, under "Lithium", p. 114; "Sodium", p. 304, "Potassium", p. 344; "Rubidium", p. 133.). Thus, it is possible, even in this connection, to interpret the strength of these bases by the ability to bind acids.

If one takes the structural viewpoint, one must relate the various stages of acidity in the case of different cations to their effective radii and charges, i.e., their field strengths. However, just these configurations as determined by ionic radii and electrostatic attractions (and deformabilities) and the resulting more or less strongly bound ion groupings, define the "acids" and "bases" of the chemist.

** Unfortunately, only too few borate and phosphate systems have been investigated to allow for analogous considerations.

Molar ratio SiO₂/base for the
highest degree of acidification

(continued)

The ability to bind SiO_2 and to form more or less stable crystalline compounds increases from top to bottom for the basic oxides we have listed. Thus, their basicity, too, increases downward in the same manner. This appears reasonable from the chemical viewpoint, since the ordering is almost always the same as that of the strengths of these bases in hydrous solutions. For example, the alkali hydroxides are stronger bases than the alkaline-earth hydroxides, and within each of these groups the basicity increases with atomic weight or ionic radius, respectively.

barium is able to form two compounds that are somewhat richer in SiO_2 , namely, $2\text{BaO} \cdot 3\text{SiO}_2$ with a congruent melting point, and $\text{BaO} \cdot 2\text{SiO}_2$ which, however, is not sufficiently stable any more as indicated by its incongruent melting point. This behavior parallels very well the increasing basicity (or ionic radius) from MgO to BaO . The third group consists of the alkalis, starting with lithium disilicate which is not very stable, to sodium disilicate and potassium tetrasilicate; the last one has the highest degree of siliconization among the simple compounds known to date. Hence, we find K_2O to be the strongest base even among the silicate systems; little is known so far about Rb_2O and Cs_2O . A remark by G. W. Morey and N. L. Bowen [9] is of interest in this connection; they state that the thermal dissociation of the alkali disilicates decreases strongly with increasing atomic weight of the alkali metal.

One can extend the above ordering of basicities into the acid range. Examples for this are the oxides of Fe^{3+} , Cr^{6+} , and others which we know to be able to act as acids in glasses; according to our discussion of basicities, one expects acid characteristics for Fe_2O_3 or CrO_3 , since neither Fe_2O_3 and SiO_2 , nor CrO_3 and SiO_2 form any compounds, whereas they are compounds of the base FeO with SiO_2 .

2. Slagging properties and basicity. There are certain relations between the arguments in our above discussion and the observations by H. Salmang [8] concerning the slagging ability of various oxides. He concludes that at 1400° , only basic oxides and basic silicates with a ratio of $\text{RO} : \text{SiO}_2$ above unity attack, for instance, fireproof materials. "Neutral silicates" with the formula $\text{RO} : \text{SiO}_2$ /301 or with an even higher content of SiO_2 are much less corrosive. On the basis of this type of slagging experiment and of the characteristic behavior of various oxides, Salmang concludes that SiO_2 and P_2O_5 "must obviously be considered as acids; it is strange, however, that the same holds true of Al_2O_3 , MgO , Fe_2O_3 , Mn_2O_3 ." In another

paper with J. Kaltenbach [10], various oxides are ordered according to their corrosivity against fireproof clay, i.e., according to their basicity or acidity. Thus, basicity decreases along the progression $\text{CaO} - \text{PbO} - \text{BaO} - \text{FeO} - \text{SnO} - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{SiO}_2 - \text{ZnO} - \text{SnO}_2 - \text{Cr}_2\text{O}_3$. Salmang adds, in support of his identification of the above oxides as bases or acids, the observation that vitreous acids have comparatively small expansion and thermal conductivity coefficients, whereas the vitreous bases show high values of these coefficients. For example, the oxides we discussed before have the following cubic expansion coefficient (according to English and Turner) in order of increasing basicity:

SiO_2	$0,15 \cdot 10^{-7}$	} acid oxides
ZnO	$0,21 \cdot 10^{-7}$	
Al_2O_3	$0,52 \cdot 10^{-7}$	
MgO	$1,35 \cdot 10^{-7}$	} weak bases
CaO	$4,9 \cdot 10^{-7}$	
BaO	$5,2 \cdot 10^{-7}$	
K_2O	$11,7 \cdot 10^{-7}$	} strong bases.
Na_2O	$12,9 \cdot 10^{-7}$	

It is obvious that there are only small differences by comparison with the ordering derived at on the basis of melting diagrams, and we conclude that the discussed relations fit very well together.

3. Solubility of glasses and basicity. The solubility of a glass by water is intimately related to its molecular structure. One expects, in the case of simple silicate glasses, that the glasses with higher basicity in the glass melt show a comparatively higher solubility, and that this degree of solubility is independent of the content of basic oxide, since both phenomena are due to the fact that the various alkali ions are bound by the remaining glass oxides, in particular, the acids, to a varying degree. This is certainly true for silicate glasses, since here we know that mostly the basic constituent is affected by water solubility, whereas the silicic lattice is barely affected. In this respect, the investigations of glass solubility permit a clear comparison, at least between sodium

and potassium silicate glasses. C. I. Peddle [11], for instance, has found the following weight losses in units of mg/100 g glass, with the measurements done on glass sand in uniform fashion:

100	mol	SiO ₂	*	+ 40	mol	Na ₂ O	24854 mgr/100 gr	Sand
100	"	SiO ₂		+ 40	"	K ₂ O	58870 mgr/100 gr	"
100	"	SiO ₂		+ 20	"	Na ₂ O	2662 mgr/100 gr	"
100	"	SiO ₂		+ 20	"	K ₂ O	5494 mgr/100 gr	"

* Those glasses contained in addition 3% CaO.

In another series of experiments, C. I. Peddle [12] compared potassium with sodium lead glasses. Again, if one compares the solubility values of the potassium glasses with those of the sodium glasses on the basis of weight, the values are the same; however, the potassium values are much higher than the sodium values, if one compares equal molar percentages of K₂O and Na₂O. It is not possible to draw more detailed conclusions, since the series was changed according to weight percentages, and since on translation into molar percentages, the lead content is somewhat shifted. However, it is interesting to note that a parallel series with only 10% alkali content shows a strong shift, in the sense that potassium glass with 10% K₂O according to weight (8.5 mole percent) is much better than the corresponding sodium glass with 10% Na₂O according to weight (12.5 mole percent). In the framework of our considerations, this means that for lower alkali content, the potassium glass is less basic by comparison with sodium glass, whereas for higher alkali content, the potassium glass is much more basic by comparison with sodium glass; we shall return to this point later.

A direct comparison of lead-free and lead-containing alkali-silicate glasses can be made on the basis of investigations by H. Karmaus [13]. He lists the following amounts of leached matter found according to Keppeler's sand test:

Molar composition
of glasses

Leached matter in units of
mg/20 g sand

Na ₂ O, 6SiO ₂
K ₂ O, 6SiO ₂
2 (PbO, SiO ₂) + 8 (Na ₂ O, 6SiO ₂)
2 (PbO, SiO ₂) + 8 (K ₂ O, 6SiO ₂)
5 (PbO, SiO ₂) + 5 (Na ₂ O, 6SiO ₂)
5 (PbO, SiO ₂) + 5 (K ₂ O, 6SiO ₂)

4410
Glass completely decomposed
120
2096
19.3
23.6

Again, we find greater solubility of potassium glasses by comparison with sodium glasses, and conclude that the latter have higher basicity.

4. Gas absorption and basicity. Another interesting comparison is due to melting experiments with simple alkali silicate glasses at high CO₂ pressures; these experiments are due to W. Weyl [14]. He found that there exists a true chemical equilibrium between carbonates and silicates in the melt. For instance, at 750 atm CO₂ and 1150° C,

0.2% CO ₂	was dissolved in	lithium metasilicate glass,
6.3% CO ₂	"	" sodium metasilicate glass,
7.9% CO ₂	"	" potassium metasilicate glass.

It is now obvious that the CO₂ absorption increases in the systems SiO₂ - Na₂O and SiO₂ - K₂O with increasing alkali content, that is, increasing basicity. Hence, among the metasilicates, the potassium glass has the highest basicity because of its increased CO₂ absorption, whereas the lithium glass is the most acid one. This is in agreement with the observations by P. Niggli [15], who found the CO₂ losses in melts of K₂CO₃ or Na₂CO₃ with SiO₂ or TiO₂, respectively, at 960° (numerical values in equivalents):

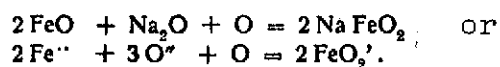
System K ₂ O - SiO ₂ - CO ₂	0.85	mol CO ₂ loss
System Na ₂ O - SiO ₂ - CO ₂	1.35	" " "
System K ₂ O - TiO ₂ - CO ₂	0.64	" " "
System Na ₂ O - TiO ₂ - CO ₂	0.82	" " "

Hence, we see that the sodium systems expel more CO_2 , and this indicates a higher acidity by comparison with the potassium systems. At the same time, the above table suggests that SiO_2 is a stronger acid than TiO_2 . This conclusion, in turn, is in agreement with the fact that in the stage of highest acidification not only $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ exists in crystalline form, but only one compound $\text{Na}_2\text{O} \cdot 3\text{TiO}_2$.

C. Influence of basicity on glass dyes

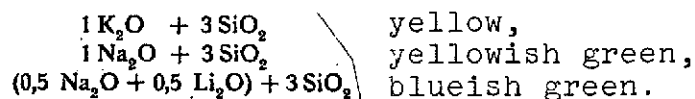
Particularly obvious is the influence of different melt basicities on glass dyes. In almost all cases, those elements are affected which may occur in the glass in two or more stages of oxidation. The higher oxidation stage is more acid, i.e., it is formed preferentially in basic melts; the lower oxidation stage (base) is formed in acid melts.

1. Iron oxide. It is well known that the color of iron glasses changes with the oxidation stage of Fe, if (with the same melting temperature, the same amount of iron oxide, and the same melting atmosphere) the alkali content of the basic glass and its basicity are changed. Chr. Andresen-Kraft [16], and N. E. Densem and W. E. S. Turner [17] have found that increasing the alkali content changes the color of the glass from green to yellow (in the sense of a Fe_2O_3 formation), whereas the color changes to blueish-green with decreasing alkali content (FeO). According to P. Csaki and A. Dietzel [18], the Fe^{II} in the glass exists as Fe^{++} cation, whereas the Fe^{III} — predominantly as $(\text{FeO}_2)^-$ anion. Thus, we can write:



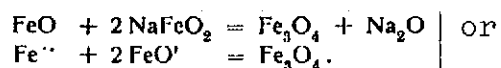
This scheme expresses particularly well the sensitivity of the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ equilibrium in the glass as a function of alkaline influences. Thus, if the iron oxide responds in this fashion to variation

in the basicity of the melt, then it should similarly respond to variations in the strength of the bases. That, indeed, is the case: if one melts an alkali silicate glass with 1% Fe_2O_3 in the platinum oven at 1400° in air, different colors are obtained according to the type of alkali used. Thus the glass:



It follows that with equal molar composition, the potassium glass is the most basic, while the Li_2O -containing glass is the most acid of the three; hence, we find the basicity to increase along the sequence $\text{Li} - \text{Na} - \text{K}$, in agreement with our previous discussion.

P. Csaki and A. Dietzel have found that, in addition, iron oxides are able to form Fe_3O_4 in glasses. This reaction sequence reads:



We see that this reaction, too, is sensitive to basicity, since the weaker base FeO is exchanged with the stronger base Na_2O . As a matter of fact, Fe_3O_4 is not found in ordinary silicate glasses, as they are already too basic. It can be easily obtained, however, for example, in the acid boric-acid-borax glasses with less than about 30 to 25% Na_2O by weight, and it is found the more the lower the content of alkali. This behavior has already been noted by the authors. It means that we now even may compare different glass-forming systems. We shall use this "indicator" later.

2. Chromium oxide. Chromium, too, changes its oxidation stage and with it, the color according to the basicity of the melt, as was discussed by W. Weyl and E. Thümen [19]. Keeping the other conditions the same, one finds predominantly the chromate ion in

alkali-rich melts, the chromic ion in acid melts. More chromate is formed in a potassium trisilicate glass than in the sodium glass of equal molar composition.

3. Vanadium oxide. As far as glass-staining is concerned, vanadium and chromium are very similar. According to investigations by W. Weyl, A. Pincus, and A. Badger [20], vanadium in the form of a trivalent cation stains green; as a 5-valent anion, it stains yellow. As before, in the cases of iron and chromium, it is possible to change the equilibrium $V^{3+} - V^{5+}$, by changing the basicity of the fundamental glass composition while keeping melting temperature and atmosphere constant.

4. Selenium. Other examples for the influence of basicity were given by W. Höfler [21] and, in particular, by W. Hirsch and A. Dietzel [22]. If selenium or a selenide is molten in neutral atmosphere with soda, a colorless crystal mass is obtained in which the selenium exists both in the form of selenides and selenites. We have:

$$3\text{Se} + 3\text{Na}_2\text{O} \rightleftharpoons \text{Na}_2\text{SeO}_3 + 2\text{Na}_2\text{Se}.$$

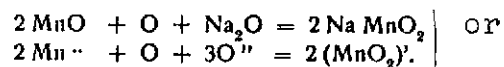
If one adds to such a melt an increasing amount of sand, that is, if one increases the acidity, then one first observes the development of a brownish color, since the equilibrium changes from right to left. However, the selenium that is formed still finds enough Na_2Se to transpose itself completely into brown-staining polyselenide. Adding additional sand results in an ever-increasing amount of free selenium which at first appears as dye in addition to the polyselenide. This is the case with silicate glasses of 20 - 25% alkali content, and they have the color of a fairly brownish selenium pink. Glasses with still less alkali (15% alkali or less) finally show the pure selenium pink with no brownish stain, which means that now the polyselenide formation has stopped. Note that the color of potassium glasses is a purer pink than that of sodium glasses; this, however, has to do with the fact that one normally replaces Na by K according to weight. If the exchange is made on the basis of molar percent, the discrepancy disappears (see Höfler [21]).

5. Sulfur. The behavior of sulfur in glasses is similar to that of selenium. In the right composition, one can obtain blue-staining free sulfur, analogous to the presence of pink-staining selenium. The most remarkable difference between selenium and sulfur is the requirement of a higher acidity for the appearance of sulfur blue by comparison with selenium. The sulfur blue forms in a sodium borate glass, for instance, at about 25% Na_2O . It is apparently impossible to obtain sulfur blue in pure silicate glasses; they seem to be too basic. We recognize the phenomenon already discussed in the case of Fe_3O_4 : According to investigations by A. Dietzel [23], the observation that sulfur blue is only obtained in melts that are more acid than melts that show selenium is qualitatively compatible with observations in hydrous solutions. If one starts with solutions of $\text{Na}_2\text{Se} + \text{Na}_2\text{SeO}_3$ or $\text{Na}_2\text{S} + \text{Na}_2\text{SO}_3$ with a strong NaOH content and slowly adds diluted HCl, then selenium is precipitated at a pH value of 10.5, whereas sulfur precipitation starts only at a pH value of 9 to 9.5; tellurium already precipitates at $\text{pH} = 13$.

6. Iron sulfides. The recent investigations by C. Neumann and A. Dietzel [24] have shown that the same rules we discussed for iron oxides determine the behavior of the so-called "carbon yellow" in melts containing iron and sulfur. Thus, if the melts are rich in alkali, sulfoferrite anions $(\text{FeS}_2)'$ are formed which yield stains of a yellow to reddish brown color. In glasses of the alkali-poor silicate, borosilicate, or borate types, this dye, as well as the corresponding oxiferrite, is not stable; instead, we have only FeS that precipitates at lower temperatures in colloidal form, resulting in gray to black staining. In technical glasses with a medium alkali content, sulfoferrite anions and FeS are both formed, and this results in stains of more or less grayish color and, thus, a dull yellowish brown. This state corresponds to the mixture of FeO blue and of Fe_2O_3 yellow, i.e., the well known iron-green in purely oxidic systems.

7. Titanium oxide. Most recently, another reaction has been found that is sensitive to the basicity of the glass (cf. R. Boncke and A. Dietzel [25]). If TiO_2 is molten into ordinary technical glass, then a colorless melt is obtained, provided other metal oxides (iron!) are excluded. If one now turns to silicate melts that are alkali-poor or, in particular, contain clay or boric acid or — even more so — if one turns to phosphate glasses, then the characteristic blue violet stain of the Ti^{3+} ion appears, provided the other melting conditions are not changed. Again, the explanation is the equilibrium between the titanium cation and the anion of the titanous acid, and this equilibrium depends on the basicity of the glass.

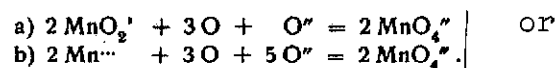
8. Manganese oxide. The manganese oxides, too, belong here, and they show in addition to the color indicators discussed so far yet another phenomenon. Until recently, only Mn^{II} and Mn^{III} were known in vitreous melts. The former does practically not stain (there is a very weak yellow color); the latter produces the well known manganese violet. Analogous to the case with iron, we can write



This reaction depends, in a similar fashion as the iron reaction, on the alkali content. If one melts into borate glasses manganese oxide (either MnCO_3 or MnO_2) in amounts of 0.1% Mn, then a lilac stain is obtained, for instance at 15 Na_2O , 85% B_2O_3 , and the intensity of this stain increases markedly if the alkali content is increased from 20 - 30%. This phenomenon can only be explained on the basis of an increase of the Mn^{III} content. Another explanation, for example, assuming the presence of Mn^{III} cations, is not compatible with this color change.

However, it was possible to obtain an additional oxidation stage of manganese in vitreous melts. This occurred when we were

looking for a color indicator in the highly basic region (see below) in which the normal indicators have long since changed color. At that time, manganese was tested which, for instance, yields in oxidizing soda preparations the well known blueish-green color of the manganese ions. It was, indeed, possible to obtain melts of 11 g soda, 3.5 g sand, and 0.01 g MnO_2 in air, which produced a blueish-green glass with a color similar to copper stain if the cooling was fast. This coloration is due to the MnO_4^- ion and occurs only in melts with this high alkali content. If the acid content is systematically increased (SiO_2 , B_2O_3 , etc.), then the color turns soon into a brownish violet (Mn^{III}). Hence, the melts with stable manganate ions must be much more basic than melts in which, for instance, Mn^{III} becomes unstable at lower basicities. Formulating the transition of Mn^{III} into Mn^{IV} , one may, in principle, consider the Mn^{III} ion as either anion or cation:



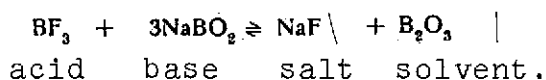
It is obvious that in case b), the transition $\text{Mn}^{\text{III}} - \text{Mn}^{\text{IV}}$ should occur very easily, since here a change in the concentration of oxygen ions and, hence, in the basicity enters to the fifth power. This, however, is not the case. Instead, the correct formulation follows the scheme we preferred in the discussion of the $\text{Mn}^{\text{II}} - \text{Mn}^{\text{III}}$ transition, that is, the interpretation of the Mn^{III} and MnO_2' anion: According to case a), a change in basicity (C_0'') enters only to the first power, that is, C_0'' must be changed quite significantly in order to effect the transition.

All these examples show that vitreous melts are by no means simply salt melts. In the following, we now first address ourselves to the question whether our concept of SiO_2 , B_2O_3 , etc., in the role of the solvent is compatible with experimental data.

III. Experimental Part

A. Are SiO_2 , B_2O_3 , etc., "solvents"?

The assumption is fascinating that SiO_2 , B_2O_3 , etc., play the role of water in vitreous melts. Thus, P. Niggli [27] concludes, on the basis of his investigations of equilibria in the systems $\text{R}_2\text{O} - \text{SiO}_2 - \text{CO}_2$ and $\text{R}_2\text{O} - \text{TiO}_2 - \text{CO}_2$, that the formation of alkali titanates or silicates in melts is not comparable to salt formation in hydrous solutions; on the contrary, the role of SiO_2 or TiO_2 is comparable to that of water, and the silicates with different SiO_2 content are analogous to the compounds that contain water of crystallization. W. Weyl [28], too, often speaks in his papers on solvation processes in glasses of the addition of neutral SiO_2 as solvent molecule. The comparison with water can be extended, in that pure silicic acid, boric acid, etc., are weakly dissociated, while material "in solution", such as Na_2O , is more or less highly dissociated. Admittedly, the low value of the dielectric constant of SiO_2 and B_2O_3 by comparison with H_2O is a problem, and, in particular, the question as to the constitution of an acid. However, one might assume the acids to be represented by molecules, such as SiF_4 , BF_3 , B_2S_3 , BN , etc. A neutralization reaction, analogous to water, could then be formulated by a relation such as:



In this framework, NaBF_4 , for example, would be an acid salt.

All attempts to realize such a reaction have so far been unsuccessful. The reason is that none of those "acids" could be solved in the postulated "solvent" B_2O_3 to a degree sufficient to measure the reaction. B_2S_3 , BN were not dissolved at all, but swam as

foreign bodies in the molten boric acid. BF_3 was produced in a platinum apparatus and routed either above or through the melts, but no significant amounts of BF_3 were dissolved. Even if NaBF_4 is molten into B_2O_3 , the fluorine disappears almost completely, probably in the form of BF_3 and NaF . In order to find out whether, with a somewhat smaller diffusion of BF_3 , the basicity is at least a little shifted, measurements of conductivity and potential in the fashion of an electrometric titration were carried out. They will be summarized briefly in the following.

B. Conductivity measurements in borate melts

If one measures the conductivity of an acid solution, adding a base, one always finds a more or less pronounced kink in the curve if the neutral point or the composition of a compound is reached. Thus, one would expect that this type of study could yield indications as to the structure of vitreous melts as well. Investigations were carried out with easily accessible sodium borate glasses. The conductivity of such glasses has already been studied by S. A. Schtschukarew and R. L. Müller [29] in the temperature range $50 - 300^\circ$. They found a kink at a Na_2O content of about 5%. However, we could not use these measurements, since their temperatures were too different from our values in the $700 - 800^\circ$ range. B. Stålhane [30] published accurate measurements of melts with higher alkali contents and, moreover, in the temperature range $700 - 800^\circ$, which is of interest to us (Figure 1).

He found that the conductivity curves indeed have kinks at certain molar ratios of $\text{Na}_2\text{O} : \text{B}_2\text{O}_3$. Nevertheless, it is difficult to see an analogy between B_2O_3 and H_2O , since the NaOH dilution does not proceed in distinct steps. It is much more reasonable to interpret Stålhane's curves by neutralization of B_2O_3 by Na_2O , which one might assume to proceed in steps, similar to the behavior of polyvalent acids in hydrous solution.

To these measurements, only measurements of the conductivity of alkali-poor melts and of melts that had been treated with BF_3 had to be added, mostly in order to test for a kink in the neighborhood of the pure B_2O_3 .

The experimental setup was as follows (Figure 2). A Philips 1000 Hz generator served as oscillator, resulting in a purely sinusoidal alternating current. R was a wide-range resistor to which, preliminarily, a variable capacitor was added in a parallel circuit; the latter was supposed to compensate for the capacity of the measuring circuit, but actually did not affect the results noticeably. The measuring vessel Z consisted of a platinum crucible with hemispherical bottom and hemispherically closed platinum tube. This tube could be inserted into the vessel by means of an adjusting device with mm scale and vernier in such a fashion that the smallest distance between tube and crucible was the same at any point (Figure 2). Hence, the vessel Z with the melt under study was one of the four resistors in the bridge circuit. The resistance capacity of the vessel Z was calibrated for a certain filling height with hydrous 1/10 normal KCl solution, or with molten KCl, respectively; in this fashion, absolute conductivity values could be obtained. In order to ascertain objectivity, a reflecting galvanometer G plus rectifier in series was introduced into

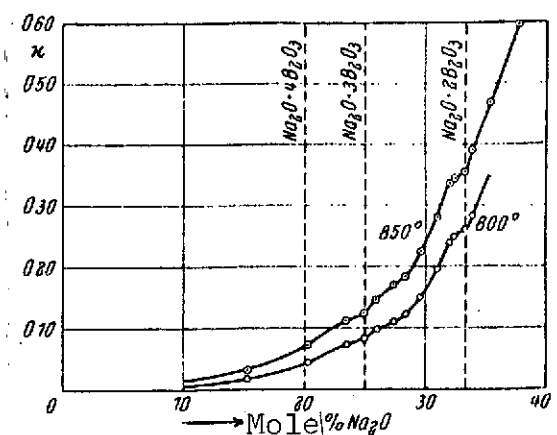


Figure 1. Electrical conductivity of sodium borate melts; according to B. Stålhane

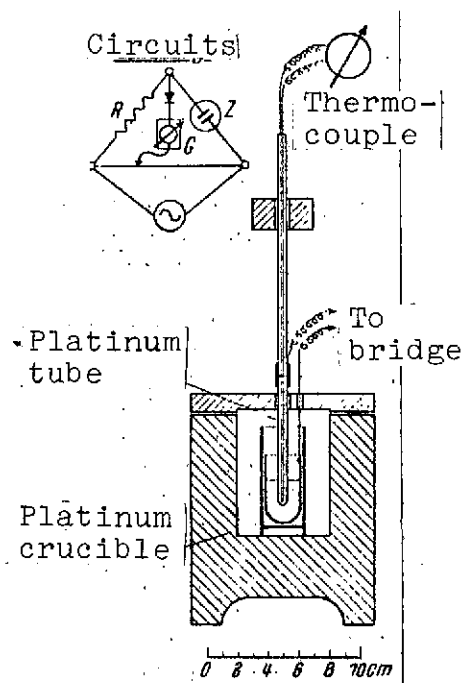


Figure 2. Experimental setup to measure conductivity

the bridge circuit. Platinization of the conductivity vessel and of the electrodes did not turn out to be very useful, since the platinum at the high temperature of the melt (700°C) was instantly dissolved, and entered the melt as a platinum sponge.

In general, the glasses were obtained in the glass-melting furnace in a platinum crucible from molten boric acid (B_2O_3 , pure melting, manufactured by E. Merck, Darmstadt), adding variable amounts of molten borax (molten borax from Schering, Berlin). The melting temperature was $900 - 950^{\circ}\text{C}$, the glasses were poured into a platinum form, and the Na_2O content determined after the conductivity measurement. The results are shown in Figure 3. In addition, the conductivity of B_2O_3 glasses into which BF_3 was introduced was measured. These results are given in Table 1.

Figure 3 shows that the kink in the curve at about a 5% Na_2O

content, as reported by Schtschukarew and Müller, is not present at the higher temperatures. Table 1 shows that the treatment of the melts with the hypothetical "acid" BF_3 does not influence conductivity to any noticeable degree. This is even true with the "solvent" B_2O_3 , as one would expect on the basis of the small solubility. Thus, in this case, too, it appears more reasonable to compare the system $\text{B}_2\text{O}_3 - \text{BF}_3$ with concentrated H_2SO_4 or with SO_3 , or, for instance, with HF that also would show only small solubility in SO_3 , in particular, at higher temperatures.

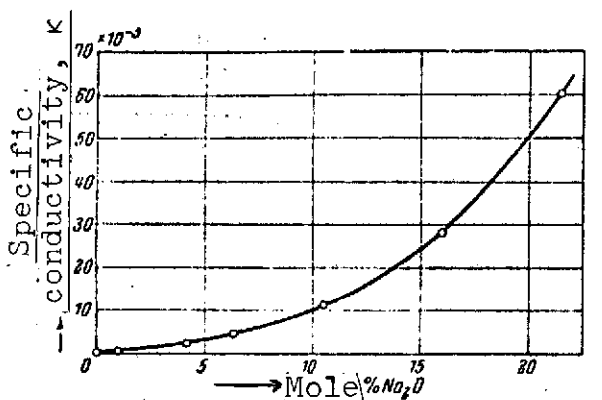


Figure 3. Electrical conductivity of alkali sodium borate glasses at 700°

TABLE 1. CONDUCTIVITY MEASUREMENTS OF DIFFERENT COMPOSITION
MELTS WHICH HAD BEEN STIRRED FOR 7 HOURS IN BF_3 GAS — TEM-
PERATURE = 700°C

	Mol % Na_2O	Mol % B_2O_3	Spec. conductivity
Treated with BF_3	0	100	$0.002 \cdot 10^{-3}$
Treated with BF_3	9.5	90.5	$13.4 \cdot 10^{-3}$
Not treated with BF_3	30.6	69.4	$113.0 \cdot 10^{-3}$
Treated with BF_3	30.6	69.4	$112.0 \cdot 10^{-3}$

It is not surprising that B_2O_3 , if interpreted as an "acid", shows low electrical conductivity and, therefore, little dissociation, since it is well known that other anhydrous acids and bases, as well as the "water-like" solvents, are dissociated to a small degree. One should not be influenced in this respect by the experience that even concentrated acids are highly dissociated in hydrous solution.

Other measurements, too, such as the potentiometric studies with the setup described below do not yield any indication that B_2O_3 behaves as a solvent. For example, if one introduces P_2O_5 into B_2O_3 , no dissociative absorption in the "solvent" occurs; on the contrary, a stable compound, completely undissociated, hard to melt and hard to dissolve, appears. This compound is commonly identified with "boryl phosphate" ($\text{BO} \cdot \text{PO}_3$ or BPO_4); chemically, it is to be understood as the anhydride of a heteropolyacid.

We may summarize that there is no reason to identify SiO_2 , B_2O_3 , etc., with solvents, but that all known facts are compatible with their identification as acids.

C. Investigations of basicities of various glass-forming systems

In order to obtain accurate values of the basicity of various glasses, primarily two methods have been used. In one method, one compares melts of different material systems as far as basicity is concerned; for instance, one compares sodium with potassium silicate glasses, but also silicate glasses with borate and phosphate glasses. In the other, one measures the oxygen-ion concentration directly and tries to determine its dependence on the composition.

1. Comparison of basicities by means of color indicators. We have already mentioned that the chemistry of glasses knows quite a few dyes that can be used to indicate basicities. In their application, however, it must be realized that their color transitions may depend on various parameters other than just basicity. Among these parameters we have, in particular, the melting temperature and internal partial pressure of oxygen in the melt*. The latter depends, in turn, on the dissociation behavior of the dye, the melting atmosphere and the duration of the melting. If one wants to compare basicities, one must, therefore, keep those other parameters constant. In earlier studies concerned with dyes, this problem was either disregarded, or the authors experimented under different conditions**, so that for our purposes their observations of dyes could not be used. In addition, the majority of experiments involved silicate glasses, and only a few used borate or phosphate systems. Thus, a basicity comparison of different glasses could only be made with specifically made melts, taking the relationships we mentioned into account.

* H. Jebsen-Marwedel and A. Becker (Sprechsaal Keramik, usw., Vol. 63, 1930, pp. 874-878 [Ref. Glastechn. Ber., Vol. 9, 1931, p. 174]), were the first to point out the fundamental importance of the "internal oxygen pressure"; for measurements of the internal oxygen partial pressure, see P. Csaki and A. Dietzel (Glastechn. Ber., Vol. 18, 1940, p. 33).

** For this reason, the melting temperature was kept higher with silicate glasses than, for instance, with borate glasses.

We have investigated sodium and potassium glasses, and in each case, silicate, borate, and phosphate systems. A color indicator was introduced into these melts and the range of compounds determined in which the color transition of the indicator occurred.

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2. Execution of the experiment. In comparing silicate with borate or phosphate glasses, the melting temperature must be kept constant in all cases. Thus, we had to select it so that all glasses within a comparative large range of compositions could be molten at the same reference temperature. This condition resulted in considerable experimental difficulties. It turned out that it would have been desirable to consider, in the case of silicate glasses, sodium contents below 20 - 15% by weight with the corresponding melting temperatures of 1300° C, and more. In the borate and phosphate systems, on the other hand, alkali contents of 50 and 60% were necessary, and these are unpleasant to work with at temperatures of more than 1300°. As a result, we left out the extreme ranges of color transition and chose uniformly a temperature of 1100° C. At this temperature, most silicate glasses could still be molten, whereas the vapor pressure of the alkali in the extremely fluid borate and phosphate glasses was not yet so high that the melt composition changed too rapidly. At the same time, the glasses did not yet corrode the furnace material and the platinum instruments too much.

In order to keep the melting atmosphere both well-defined and constant, it appeared easiest to use air. There was the additional condition that the oxygen partial pressure of the melts had to be identical to that of the air. This was achieved by keeping the melts long enough at the experimental temperature, and also by stirring them in an appropriate manner to ensure equilibrium with the gaseous phase. This was particularly important in the case of the relatively viscous silicate glasses, but also in some potassium borate melts. In practice, we premelted the melts at an appropriate temperature which was chosen in accordance with the melting behavior of the substances in question, and then poured the melt out to form little fragments. The fragments were then introduced into a platinum drum.

(Figure 4), which was rotated in the electric furnace at 1100° C until oxidation equilibrium with the air atmosphere was reached. The stirring time was determined from test samples which were obtained by introducing, for example, the manganese oxide in one melt in the form of MnCO_3 , in another in the form of KMnO_4 ; the small amounts of potassium that were introduced through the permanganate could be disregarded. Both melts had to have the same color intensity. After the melting process, the glass was poured in air from the drum into some mold, resulting in laminae of 20 mm

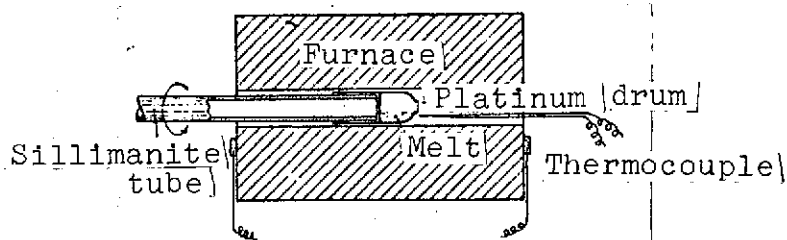


Figure 4. Stirring device to obtain the melts

by 20 mm to judge the color*, or else the drum was rotated with the furnace to a vertical position, and the glass was poured into a porcelain vessel. The latter method had to be used with the very viscous silicate melts. A corrosion of the porcelain container was not likely at 1100° C in a short time and, moreover, the edge areas of the laminae were removed in grinding and polishing. In the case of highly fluid borate and phosphate melts, this procedure was unnecessary. These melts were kept in the platinum crucible at 1100° C, and, in a sense, titrated until the color transition point was reached, i.e., a certain transition color, by adding alkali, B_2O_3 , or vitreous metaphosphoric acid. The color development could be easily followed by extracting test samples with a platinum stirrer. Finally, the melt was poured out and the alkali content determined.

The color transition region was determined in each of the three systems by adding three color indicators, namely, CrO_3 , V_2O_5 , and

* In general, a spectrophotometric measurement was unnecessary, since the complete transition was almost always effected within about a 5% change of alkali content; the comparison of two glasses was carried out with a 1 or 2% accuracy, since color equality in the transition region was checked.

Mn_2O_3 , and by systematically changing the alkali content.

In the case of chromium, the transition $\text{Cr}^{\text{III}} - \text{Cr}^{\text{VI}}$, in the case of vanadium, the transition $\text{V}^{\text{III}} - \text{V}^{\text{V}}$, and in the case of manganese $\text{Mn}^{\text{III}} - \text{Mn}^{\text{VI}}$, was used as indicator for the basicity; the transition mechanism of the latter is discussed above.

In another test series, we compared, in addition, lithium, sodium, and potassium borate glasses with Fe_3O_4 as indicator. Here, the basicity is characterized by a more or less grayish color (Fe_3O_4), and the comparison was made with the aid of extinction measurements at 650 μm . At this wavelength, the absorption of the yellow-staining Fe^{III} , present in addition to Fe_3O_4 , is already rather small and could be neglected, since iron content and thickness of laminae were identical for all glasses. Hence, equal extinction indicated equal basicity.

III. Results

Chromium oxide as indicator

$\text{Na}_2\text{O} - \text{SiO}_2$ melts with 25% and 20% Na_2O showed the chromate yellow color (lemon color). Melts with a lower sodium content could not be obtained at 1100°. The transition to chromium green was, therefore, not observable. It occurs probably at about 15% Na_2O or below. (All percentages are by weight).

$\text{K}_2\text{O} - \text{SiO}_2$ glasses were so hard to melt at 1100° that they could not be used.

$\text{Na}_2\text{O} - \text{B}_2\text{O}_3$ melts with 15%, 20%, 25%, and 31% Na_2O (borax) were green; only the melt with 35% Na_2O was yellow. In the average, the transition occurred at 33% Na_2O .

$K_2O - B_2O_3$ melts with 10% and 15% K_2O were intensely green, with 20% K_2O yellowish green, and with 25% and 30% K_2O — yellow with a little greenish tint. The average of the transition point was 20% K_2O .

$Na_2O - P_2O_5$ compositions (from soda and vitreous metaphosphoric acid) /307 yielded the transition point yellow vs. green at a sodium content of 45% Na_2O . They were mostly crystallized.

$K_2O - P_2O_5$ compositions had their transition between 35% and 40% K_2O . We were unable to determine the transition point accurately, since these substances could only be obtained in crystalline form.

Vanadium oxide as indicator

$Na_2O - SiO_2$ melts could not be induced to turn from vanadate yellow to vanadous green at 1100°. Because of crystallization, the alkali content could not be lowered sufficiently. Similar to the case of chromium oxide, we expect it to be around 15% Na_2O or below.

$Na_2O - B_2O_3$ melts resulted in a color transition yellow to green, and we found a medium yellowish green at 35% Na_2O .

$K_2O - B_2O_3$ melts with 25% K_2O were green, with 30% yellowish green, with 36% greenish yellow. The transition of the color corresponding to the system $Na_2O - B_2O_3$ occurred at 30% K_2O .

$Na_2O - P_2O_5$ melts showed the color transition at 33% Na_2O .

$K_2O - P_2O_5$ melts changed at 37% K_2O .

Manganese oxide as indicator

$\text{Na}_2\text{CO}_3 - \text{SiO}_2$ melts had their transition from manganate yellow to manganic brownish-violet at 67% Na_2O .

$\text{K}_2\text{CO}_3 - \text{SiO}_2$ either crystallized easily in the color transition region or could not be melted at all at 1100° . The composition with 56% K_2O was still greenish-blue, the one with 47% K_2CO_3 was violet. Thus we have the transition in the average at 52% K_2O ($\pm 3\%$).

$\text{Na}_2\text{CO}_3 - \text{B}_2\text{O}_3$ melts changed at a natron content corresponding to 62% Na_2O .

$\text{K}_2\text{CO}_3 - \text{B}_2\text{O}_3$ melts had their transition at a potash content between 55 and 60% K_2O , in the average, therefore, at 57% K_2O .

$\text{Na}_2\text{CO}_3 - \text{P}_2\text{O}_5$ compositions crystallized easily. The transition region could not be determined with sufficient accuracy.

$\text{K}_2\text{CO}_3 - \text{P}_2\text{O}_5$ compositions, too, crystallized easily. The transition occurs at about 58% potash, calculated as K_2O .

Iron oxide as indicator

The measurements of the gray content, indicating Fe_3O_4 formation, resulted in the values shown in Figure 5 for the $\text{Li}_2\text{O} - \text{B}_2\text{O}_3$, $\text{Na}_2\text{O} - \text{B}_2\text{O}_3$, and $\text{K}_2\text{O} - \text{B}_2\text{O}_3$ melts.

The stated compositions are synthetic values, since in the case of sodium borate and potassium borate melts, no significant differences are expected; we have checked this point by samples. However, it was judged desirable to check the alkali content in the case of

lithium glasses, since Li_2O evaporates easily. Indeed, we have found only 4%, instead of 5% Li_2O (by weight), and only 8% — instead of 10%.

Figure 5 shows the compositions which at 1100° yield the same gray content, amount of Fe_3O_4 , and thus the basicity. Among others, these are the melts:

$\text{Li}_2\text{O}-\text{B}_2\text{O}_3$	with 17 mol % Li_2O ,
$\text{Na}_2\text{O}-\text{B}_2\text{O}_3$	with 12 mol % Na_2O ,
$\text{K}_2\text{O}-\text{B}_2\text{O}_3$	with 8 mol % K_2O .

Summarizing all these results yields an interesting review of the acidity of these systems. We have translated in Table 2 the oxide percentages in mole percentages in order to directly compare the alkalis. Boric acid is expressed as B_2O_3 , similarly — P_2O_5^* .

Compositions in the same column then have the same basicity. Let us discuss Table 2 in more detail.

If one compares the influence of the various alkalis on the transition point of the indicator, that is, the basicity, we see that in all cases, the amount of alkali necessary to reach the transition point is lowest for potash; more soda, and in some cases, much more, is needed, and of lithium oxide, which is the weakest base, the largest amount has to be added to cause the indicator to

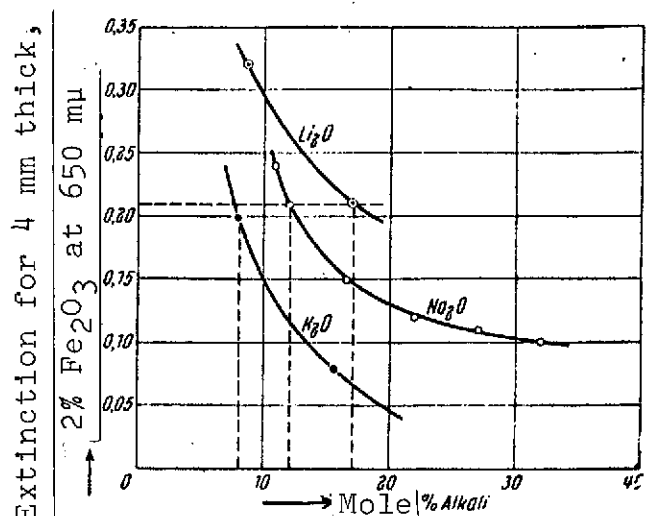


Figure 5. Gray content of Fe-containing alkali borate glasses due to Fe_3O_4 formation (1100°C)

* From the viewpoint of structural chemistry, it would be more accurate to compare 1 mol SiO_2 with $1/2$ mol B_2O_3 or P_2O_5 , rather than 1 mol B_2O_3 or P_2O_5 since the fundamental building block is in all cases $[\text{SiO}_4]$, $[\text{BO}_4]$, or $[\text{PO}_4]$. However, the usual methods involve B_2O_3 and not $1/2 \text{B}_2\text{O}_3$, and thus we did not want to change this manner of calculating.

change color. In the average, the Na_2O content (in mol %) must be 1.5 times the K_2O content in order to obtain a glass of identical basicity; in the one case studied, the ratio of Li_2O to K_2O content is even 2.1.

TABLE 2. ALKALI CONTENT AT THE COLOR TRANSITION POINTS OF THE INDICATORS
(All values in mol%)

Melt	$\text{Cr}^{\text{III}}-\text{Cr}^{\text{VI}}$	$\text{V}^{\text{III}}-\text{V}^{\text{V}}$	$\text{Mn}^{\text{II}}-\text{Mn}^{\text{VI}}$	Fe_3O_4
$\text{Na}_2\text{O}-\text{SiO}_2$	$\leq 15\%$	$\leq 15\%$	67%	—
$\text{K}_2\text{O}-\text{SiO}_2$	—	—	42%	—
$\text{Li}_2\text{O}-\text{B}_2\text{O}_3$	—	—	—	17%
$\text{Na}_2\text{O}-\text{B}_2\text{O}_3$	36%	38%	64%	12%
$\text{K}_2\text{O}-\text{B}_2\text{O}_3$	15%	24%	50%	8%
$\text{Na}_2\text{O}-\text{P}_2\text{O}_5$	65%	53%	—	—
$\text{K}_2\text{O}-\text{P}_2\text{O}_5$	46%	47%	63%	—

In addition, Table 2 allows for an interesting comparison of the acidities of the three acids SiO_2 , B_2O_3 , and P_2O_5 . One immediately sees that the transition point of chromium, vanadium (and even of iron) in the silicate systems occurs at low alkali contents, and this is in contrast to the borate and — even more so — phosphate systems. Our experiments leave no doubt that SiO_2 is the weakest acid, that B_2O_3 is already significantly more acid*, and that P_2O_5 is the strongest of the three acids.

By comparison, the manganate as indicator appears to behave somewhat differently. Whereas the potash content at the transition point shows an increase of acidity from SiO_2 to B_2O_3 to P_2O_5 , although not quite as strongly, the natron contents are of the same order for SiO_2 and B_2O_3 , and we believe that the phosphate value would not be much higher either. This remarkable fact agrees very well with the conclusions to be drawn from later, electrochemical measurements: One has to assume that in the case of such high alkali content, a state of very significant, if not almost complete dissociation, is reached; then, the differences in basicity and acidity are partly obliterated. Such a high degree of dissociation is

* This relationship changes, of course, if we compare SiO_2 moles with $1/2 \text{ B}_2\text{O}_3$ moles; see footnote, page 35. Then, the strength of boric acid is comparable to the strength of silicic acid.

reached with basic potassium glasses at a somewhat lower content of alkali than with sodium glasses.

To give a simple and clear summary of the acidity behavior, we show in Figure 6 a scheme with the values from Table 2: it shows some lines of equal acidity (isoacides).

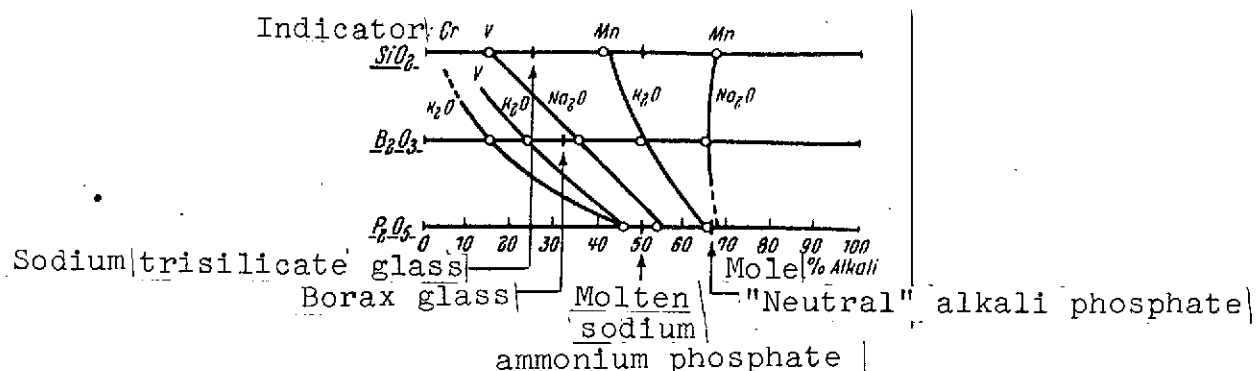


Figure 6. Lines of equal acidity (isoacides) for a melting temperature of 1100° C

We see that a trisodium trisilicate glass with 25 molar % Na₂O is more basic than a sodium diborate glass (borax) with 33% Na₂O, or a phosphate glass with 50 molar % Na₂O of the type obtained from sodium ammonium phosphate NaNH₄HPO₄ for pearl reactions. The NaNH₄HPO₄ melt has about the same basicity as the borax melt, and this is probably one reason why both lead to nearly identical phenomena in pearl reactions.

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